

PATENT SPECIFICATION

1,020,575

1,020,575



Inventors: JOHN MacLELLAND POLLOCK and
ALAN JOHN SHIPMAN.

Date of filing Complete Specification: June 25, 1962.

Application Date: July 12, 1961.

No. 25255/61

Complete Specification Published: February 23, 1966.

© Crown Copyright 1966.

Index at Acceptance:—C3 R9P.

Int. Cl.:—C 08 g.

COMPLETE SPECIFICATION

NO DRAWINGS

Preparation of Polymers of β -Lactones

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process in which carbon monoxide and a 1,2-epoxide are reacted together to give a β -lactone as the major intermediate product. Since β -lactones readily homopolymerise the final reaction product is essentially a β -lactone polymer, but polyesters may be formed at the same time in side reactions between epoxides and β -lactone.

The reactions require superatmospheric pressures and elevated temperatures to bring them about as well as the assistance of catalysts that are metal carbonyls. At the higher temperatures and pressures polyester formation is more pronounced.

According to our invention we provide a process for making β -lactone polymers comprising subjecting a mixture of a 1,2-epoxide and carbon monoxide to the action of superatmospheric pressure below about 500 atmospheres and elevated temperature below about 150°C in the presence of a metal carbonyl as catalyst.

Examples of 1,2-epoxides that undergo the various reactions are ethylene oxide, propylene oxide and styrene oxide.

Suitable catalysts are to be found among the carbonyls of iron, cobalt, nickel and chromium, of which dicobalt octacarbonyl is preferred. On the other hand, if dicobalt octacarbonyl is made in situ by adding finely-divided cobalt to the reaction mixture and allowing it to react with carbon monoxide the higher temperature required to bring about its formation seems to be

unfavourable for β -lactone formation. Catalytic amounts of water, methanol or hydrogen may be added to the reaction system to assist in the formation of cobalt carbonyl hydride which is a possible intermediate catalyst. Yields of β -lactone polymers can be increased by the addition of small amounts of promoters to the reaction system of 1,2-epoxide, carbon monoxide and metal carbonyl. Examples of such promoters are metal halides, particularly those of the alkali metals of which potassium iodide is preferred because of its better solubility in organic media; for the same reason mercuric chloride is the preferred non-alkali metal halide. Quaternary ammonium halides, for example tetraethyl ammonium bromide, are also suitable promoters. The proportion of promoter is from 0.10% to 5.0% by weight of the epoxide, usually from 0.50% to 2.0%.

There are no clear-cut limits of temperature and pressure by means of which the conditions for β -lactone formation and polyester formation may be closely defined, but it would appear that at temperatures of 80-150°C and pressures of less than 500, preferably from 50 to 300, atmospheres the reaction product consists essentially of β -lactone polymers, whilst above about 150°C and under pressures of 500-3000 atmospheres the product contains little β -lactones or their polymers but consists mainly of polyesters having molecular weights in the approximate range 100-600. Some of these polyesters derived from ethylene oxide yield formic and acetic acids on hydrolysis, which indicates that they may be polyacrylates. Acrylic acid or its esters are also likely to be present when the reaction takes place above about 200°C since it is known that β -propiolactone polymer pyrolyses to give acrylic acid. Likewise,

[Price 4s. 6d.]

if the 1,2-epoxide is propylene oxide, crotonic acid and its esters are likely to be found at the higher temperatures.

The tendency of 1,2-epoxides, especially ethylene oxide and propylene oxide to homopolymerise may be diminished by adding a small proportion of a base to the reaction mixture, for example pyridine.

The saponification number of the β -lactone polymer product is usually somewhat higher than the theoretical value because some copolymerisation with epoxide takes place. The degree of copolymerisation can be kept low by having an excess of carbon monoxide present, for example by slow injection of epoxide into the reaction system.

It is known that homopolymers of β -lactones on pyrolysis at temperatures of from about 180° to 250°C in the presence of a polymerisation inhibitor, and preferably under reduced pressure, give good yields of α - β unsaturated carboxylic acids. It is also known that α - β unsaturated esters can be made by heating a β -lactone homopolymer with an alcohol in the presence of a dehydrating agent. Thus the present process for making homopolymers of β -lactones provides a new way of obtaining α - β unsaturated acids and their esters.

The invention is illustrated by the following examples.

Example 1

100 ml. dry ethylene oxide was heated at 100°C with 1 g. dicobalt octacarbonyl at 100 atm. pressure of carbon monoxide for 1 hour, in a silver-lined pressure vessel. The pressure was then raised to 200 atm. for 1 hour, and finally to 300 atm. for 15 hours. When the vessel was cooled and the pressure released, the crude product was found to be 89 g. of viscous liquid. This product was pumped at 1 mm. at room temperature, and 26 g. of volatile components collected in a cold trap. Analysis of this fraction showed that it contained β -propiolactone together with acetaldehyde and crotonaldehyde. The β -propiolactone was separated by fractionation and its identity confirmed by its infra-red spectrum.

The product remaining after pumping at 1 mm. was distilled; only 3 g. of pale yellow liquid distilled between 35° and 80° at 1 mm. The remainder of about 60 g. was highly viscous, and was partially distilled at 0.01 mm. At the temperature necessary for distillation however some decomposition took place and the decomposition products were collected in a cold trap. Vapour-phase chromatographic analysis of these products showed that acrylic acid had been formed. The elemental analysis of the viscous liquid from which the acrylic acid was formed

was: % C, 48.8; H, 6.7; O, 42.0. β -propiolactone polymer requires % C, 50.0; H, 5.5; O, 44.5. Infra-red analysis showed it to be β -propiolactone polymer with minor impurities.

Example 2

2 g. of potassium iodide and 1 g. of water were charged to a stainless steel stirred autoclave which was then evacuated. 100 g. of ethylene oxide containing 4 g. of dicobalt octacarbonyl were then charged to the autoclave, which was then purged and charged with carbon monoxide up to 100 atmospheres. The autoclave was stirred and heated to 100°C, and the pressure then adjusted to 150 atmospheres. After 16 hours at 100°C the autoclave was cooled, excess carbon monoxide discharged, and 130 g. of brown, viscous liquid recovered. Unchanged ethylene oxide (10 g.) and a small amount of volatile aldehydes were stripped from the polymer under reduced pressure, leaving 112 g. of viscous liquid β -propiolactone polymer having a saponification number of 94 (theory for $[-O-CH_2CH_2CO-]$ is 72).

Pyrolysis of 100 g. of the β -propiolactone polymer at 200°C and 80 mms Hg pressure in the presence of cupric acetate gave 82 g. of a clear colourless liquid containing 71% of acrylic acid.

Example 3

2 g. of tetraethylammonium bromide, 1 g. of water, and 100 g. of ethylene oxide containing 4 g. dicobalt octacarbonyl were charged to an electrically-heated stirred autoclave as used in Example 2. The autoclave was heated to 120°C and pressurised to 200 atmospheres with carbon monoxide. The reaction time was 16 hours, and the yield of β -propiolactone polymer was 120 g. after 15 g. unchanged ethylene oxide had been removed under vacuum.

Pyrolysis of 100 g. of the β -propiolactone polymer as described in Example 2 gave 65 g. of colourless liquid containing 57% of acrylic acid.

Example 4

2 g. of potassium iodide, 1 g. of water and 100 g. of propylene oxide containing 4 g. of dicobalt octacarbonyl were charged to an autoclave as used in Example 2. The autoclave was heated at 100°C and pressurised to 150 atmospheres with carbon monoxide. The reaction time was 10 hours and the yield of polymeric β -butyrolactones was 118 g. after 12 g. of propylene oxide had been recovered unchanged.

Pyrolysis of 100 g. of the polymeric β -butyrolactones gave 56 g. of crude trans-crotonic acid which on distillation yielded 45 g. of trans-crotonic acid m.pt. 72°C.

WHAT WE CLAIM IS:—

1. A process for making polymers of β -lactones comprising subjecting a mixture of a 1,2-epoxide and carbon monoxide to

the action of superatmospheric pressure below about 500 atmospheres and elevated temperature below about 150°C in the presence of a metal carbonyl as catalyst.

5 2. A process as claimed in Claim 1 in which the 1.2-epoxide is ethylene oxide or propylene oxide.

10 3. A process as claimed in Claim 1 for making polymers of β -propiolactone comprising reacting ethylene oxide and carbon monoxide at pressure from 50 to 300 atmospheres and temperatures from 80° to 150°C in the presence of dicobalt octa-

15 4. A process as claimed in Claims 1, 2 and 3 in which the reaction system

of 1.2-epoxide, carbon monoxide and metal carbonyl catalyst there is added from 0.10 to 5.0% by weight of the epoxide of a promoter chosen from the group consisting of metal halides and quaternary ammonium halides.

5. A process as claimed in Claim 4 in which the promoter is potassium iodide or tetraethylammonium bromide.

25 6. A process for making polymers of β -lactones substantially as hereinbefore described and with reference to the examples.

ALFRED BALL,
Agent for the Applicants.

THIS PAGE BLANK (USPTO)